

THE INFRARED ABSORPTION SPECTRUM OF METHYL DEUTERIDE

By
NATHAN GINSBURG

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The Infrared Absorption Spectrum of Methyl Deuteride

NATHAN GINSBURG AND E. F. BARKER, *University of Michigan*

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The six fundamental vibrational frequencies of methyl deuteride were observed and the fine structure of the bands resolved. The frequencies are $\nu_6 = 1156.3$, $\nu_5 = 1306.8$, $\nu_4 = 1477.1$, $\nu_3 = 2205.25$, $\nu_1 = 2983.0$, $\nu_2 = 3031.0$. From the fine structure of the bands, the moments of inertia are found to be

$$I_A = 7.166 \times 10^{-40} \text{ g cm}^2, I_C = 5.298 \times 10^{-40} \text{ g cm}^2$$

and the internuclear distances are

$$\text{C-H} = 1.093 \times 10^{-8} \text{ cm}, \quad \text{H-H} = 1.785 \times 10^{-8} \text{ cm}.$$

From the four previously known frequencies of methane

and each of the frequencies of this molecule, the values of the five potential constants are computed. Three of the sets are consistent and agree well with the values found by Dennison and Johnston, but the other three sets have either negative or imaginary values. The frequencies from which these are calculated are the ones which take part in a resonance interaction which was not included in the theory. From the observed spacings of the zero branches of the perpendicular bands, extreme ranges of the rotation-vibration interaction factors are computed. An overtone, $2\nu_4 = 2923$, was also observed as were three frequencies of the molecule CH_2D_2 , at 1036.0, 1090.5, and 1235.5 cm^{-1} .

INTRODUCTION

THE infrared absorption spectrum of methane was first investigated by Ångström¹ and later by Coblentz,² who corrected Ångström's work. He reported bands at 2.35μ , 3.31μ , and 7.7μ . Cooley³ resolved the two longer wavelength bands into their fine structure obtaining separations of 5.4 and 9.7 wave numbers. This gave two different values for the moment of inertia when only one was expected. Neither Dennison,⁴ assuming a regular tetrahedral structure, nor Guilleman,⁵ assuming a pyramidal structure for the molecule, could give a satisfactory explanation of this.

With the discovery of the heavy isotope of hydrogen, it was possible to replace one of the H atoms of methane by a D atom and thus remove part of the degeneracy of the vibrational levels. This also introduces a preferred axis for rotation, the moment of inertia about it being the same as for normal methane.

Rosenthal⁶ was able to obtain expressions for all of the frequencies of the various isotopic methanes in terms of five potential constants and certain mass factors. The four vibrational frequencies of methane (shown in Table I)

TABLE I. The frequencies have been numbered according to the methyl halide system. α —Dennison and Johnston's computed values. β —This frequency is inactive and can be obtained only from combination bands. γ —This frequency appears in the Raman effect.

METHANE		METHYL DEUTERIDE	
		OBSERVED	CALCULATED ^{α}
ν_4	1307	B ν_6	1156.3
		A ν_5	1306.8
		D ν_4	1477.1
ν_2	(1520) ^{β}	C ν_3	2205.25
		E $2\nu_4$	2923
ν_1	(2915) ^{γ}	F ν_1	2983.0
ν_3	3012	G ν_2	3031.0
			3013

uniquely determine two of the constants, while two more are given in terms of the fifth. Thus, one of the frequencies of any of the isotopic methanes determines these three constants so that all of the other frequencies can be calculated. Dennison and Johnston⁷ were able to obtain values for these constants from consideration of the rotation-vibration interaction of normal methane. These computed constants, together with Rosenthal's equations, enabled them to calculate all the vibrational frequencies. The observed values will be compared with their computed ones later.

EXPERIMENTAL

Apparatus and procedure

Two different grating spectrometers with rock-salt fore prism were used in this investigation.

⁷ Dennison and Johnston, *Phys. Rev.* **47**, 93 (1935).

¹ Ångström, *Ofversigt af Kongl. Vetenskaps-Akad. Forh.* **47**, 331 (1890).

² Coblentz, *Investigations of Infrared Spectra*, p. 43 and Diagram 12.

³ J. P. Cooley, *Astrophys. J.* **62**, 73 (1925).

⁴ D. M. Dennison, *Astrophys. J.* **62**, 84 (1925).

⁵ V. Guilleman, *Ann. d. Physik* **81**, 173 (1926).

⁶ J. Rosenthal, *Phys. Rev.* **45**, 538 (1934).

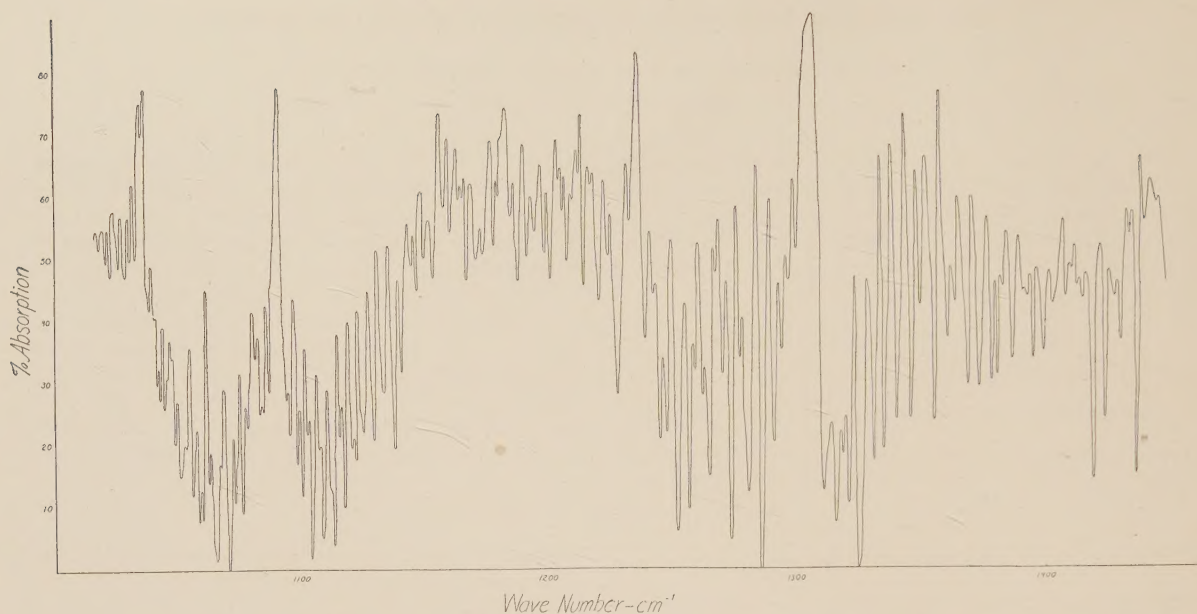


FIG. 1.

The one built and described by Barker and Meyer⁸ was used with a Moll-Burger relay, the galvanometer being read at a distance of four meters; the second was built by Hardy⁹ with a Pfund thermoelectric amplifier, the galvanometer being read at a distance of three meters. Two gratings were used, a 2400-line per inch grating in the 6 to 10μ region, and a 4800-line per inch grating in the 3 to 5μ region. A ten-cm glass cell, in the shape of two elliptical cones placed apex to apex, was used in order to get maximum absorption with the small amount of gas available. After more gas was made, a twenty-five cm elliptical glass cell with rocksalt windows was used. The source of the continuous radiation was a Nernst glower.

The procedure is as follows: With the cell in the beam, the slit widths are adjusted to give maximum deflection with good resolution. The grating is set at equal intervals throughout the spectral region under examination. Readings are taken with the cell in the beam and out of it, at least three being taken at each setting of the grating. Then the percent absorption is plotted against the frequency as determined

from the grating relation $1/\nu = k \sin \theta$, where θ is the angle from the central image and k is the spectrometer constant. The position of the central image is determined at the beginning and end of each run. The spectrometer constants were known from previous work, but were rechecked. Each band was mapped at least twice, the results being in very good agreement.

Exploratory measurements

A sample of gas was obtained from W. A. Webb which contained a mixture of methyl deuterides, mostly CH_3D . With the 10-cm cell, the absorption spectrum was mapped in the regions from 6μ to 10μ and from 3μ to 3.5μ . Five very prominent bands were found in the long wave region (Fig. 1) with centers at 1036.0, 1090.5, 1156.5, 1235.5 and 1306.7 cm^{-1} . In the 3.3μ region, only one band was found, its center being at 3013 wave numbers. This, and the one at 1306.7 cm^{-1} , were identified as ν_3 and ν_4 of normal methane since the spacings of the fine structure are the same as those found by Cooley. The 1036 and 1235 cm^{-1} bands were identified as belonging to the CH_2D_2 molecule because of their irregular fine structure, which would be expected from an asymmetric rotator. The other

⁸ Barker and Meyer, Trans. Faraday Soc. 25, 913 (1929).

⁹ J. Hardy, Phys. Rev. 38, 2162 (1931).

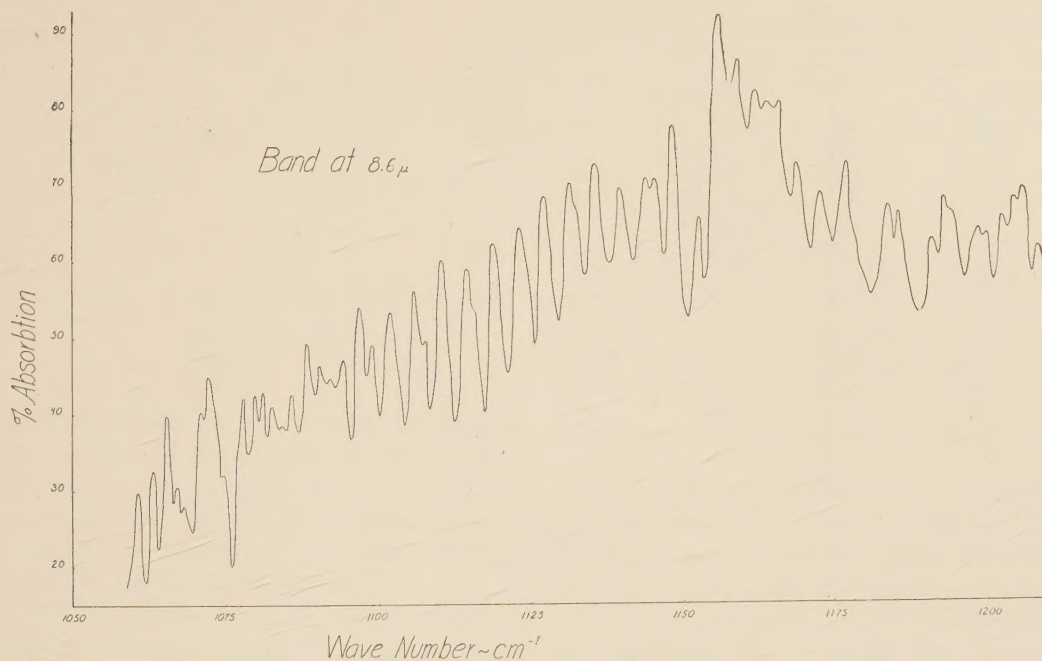
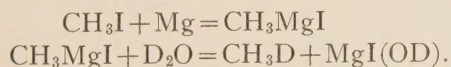


FIG. 2.

two bands were temporarily identified as ν_5 , a parallel band,¹⁰ and ν_6 , a perpendicular band, of CH_3D . Calculations were then made with $\nu_5 = 1090$ to obtain the fifth potential constant which is required to solve the equations for the other vibrational frequencies. None of the frequencies so computed could be identified with the observed bands. Because of this ambiguity in the identification of the bands of the various methanes present in the mixture, it was necessary to prepare a new sample of gas by a method which gives methyl deuteride in a much higher concentration.

Preparation of the gas

A new supply of gas was prepared by means of the Grignard process, using heavy water.



Dibutyl ether, rather than ethyl ether, was used as the solvent for the Grignard reagent because it is less volatile. In order to remove the small amount of ether vapor that came over in spite

of all precautions, the gas was collected over concentrated sulphuric acid.

On spectroscopic examination of this gas, the bands of CH_2D_2 were again observed but with so much smaller intensity that they did not prove annoying. The band at 1090 cm^{-1} was also very weak and consequently was identified as belonging to the CH_2D_2 molecule. There was a small percentage of normal methane present too.

Results

Six fundamental frequencies are expected for the CH_3D molecule. Three of these will be parallel and single, and three will be perpendicular and double. Each of the triple frequencies of normal methane splits up into a parallel and a perpendicular band, just as in the case of the methyl halides. However, the methyl halides have as their lowest frequency a parallel vibration and then alternating perpendicular and parallel bands, while this molecule has as its lowest frequency band a perpendicular vibration. All six of the bands were observed, together with their fine structure. Their frequencies are given in Table I and are compared with Dennison and

¹⁰ Barker and Ginsburg, J. Chem. Phys. 2, 299 (1934).

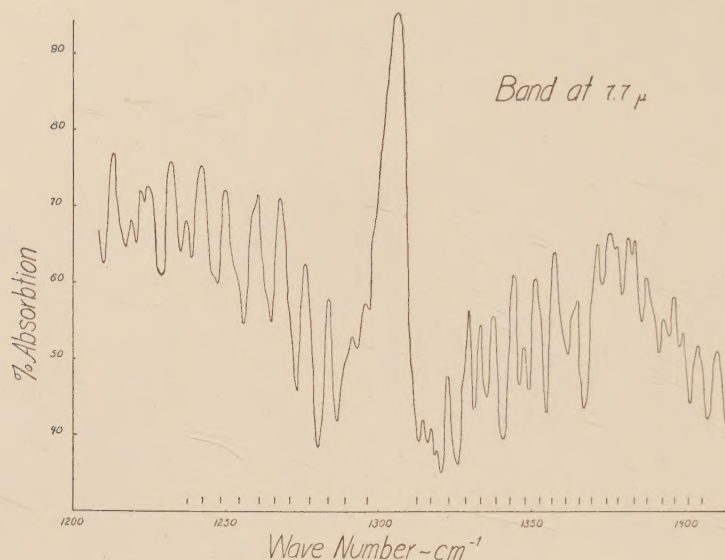


FIG. 3.

Johnston's calculated values. The location of the overtone is somewhat doubtful.

The lowest frequency band is ν_6 , with the maximum at 1156.3 wave numbers (Fig. 2). The fine structure has a very regular spacing, with separations ranging from 3.8 to 4.5 wave numbers (Table II). An unusual feature of this band is the "hole" on the low frequency side of the center. Measurements were not extended to higher frequencies because of the overlapping of the 1307 cm^{-1} band.

The parallel band, $\nu_5 = 1306.8 \text{ cm}^{-1}$, has almost the same frequency as ν_4 of normal methane, consequently there is some overlapping. The

positions of the methane lines are marked on the absorption curve (Fig. 3) and correspond exactly to some of the observed lines (Table III). The separation between lines near the center of the band, where the overlapping is less marked, is about 7.7 cm^{-1} .

A second perpendicular band, ν_4 , appears just on the high frequency side of the parallel band. It is not as intense as the others and lies

TABLE III. The fine structure of ν_5 showing the overlapping of the normal methane band, ν_4 .

POSITIVE BRANCH CH ₃ D		NEGATIVE BRANCH CH ₃ D	
1156.3	1156.3	1295.4	1295.5
1159.4	1152.7	1291.1	
1162.3	1148.6	1283.3	1283.5
1164.0	1145.4	1275.6	
1166.1	1144.0	1267.3	
1168.9	1139.6	1259.7	
1172.8	1135.5	1249.6	
1176.8	1131.4	1241.9	
1184.0	1127.3	1236.9	
1185.6	1123.1	1231.8	
1191.2	1118.9	1224.1	
1193.1	1114.6	1222.0	
1198.7	1110.3	1218.8	
1200.2	1105.7	1213.0	
1202.6	1101.8		

POSITIVE BRANCH CH ₃ D		NEGATIVE BRANCH CH ₄	
1314.2		1317.2	
1317.0			
1319.0			
1322.1			
1329.2			
1333.1	1333.2		
1337.2			
1343.6			
1347.3	1347.5		
1351.1			
1357.0	1356.7		
1364.5			
1371.0			
1375.1	1375.0		
1377.5			
1381.0			
1383.0	1383.2		
1386.8			
1392.7	1392.6		
1396.3	1396.4		
1398.8			
1403.6			
1410.0			

TABLE II. The fine structure lines of the perpendicular band ν_6 . The irregularity in the positive branch is due to the overlapping of ν_5 .

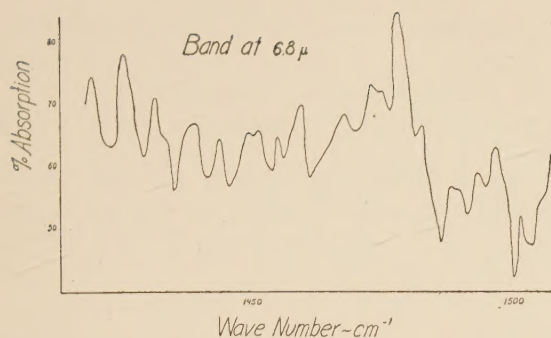


FIG. 4.

in the midst of the 6μ water vapor absorption region, making it very difficult to measure. It, too, has a "hole" near the center of the band, but on the high frequency side (Fig. 4). The spacing is somewhat irregular, varying between five and six wave numbers.

The second parallel band, ν_3 , has its center at 2205.25 cm^{-1} (Fig. 5). Since this region is free of other bands, it could be very accurately measured. The fine structure lines are very regularly spaced, so that the formula

$$\nu_m = 2202.25 + 7.714m - 0.0434m^2$$

could be fitted to them. The observed frequencies of these lines together with their differences from the calculated values are given in Table IV. The increased absorption on the high frequency side is due to the CO_2 of the atmosphere.

TABLE IV. The frequencies of the parallel band, ν_3 .

m	POSITIVE BRANCH		NEGATIVE BRANCH	
	OBSERVED	Δ	OBSERVED	Δ
1	2212.0	-0.91	2196.75	-0.75
2	2220.4	-0.10	2190.1	+0.43
3	2227.6	-0.42	2181.7	-0.03
4	2235.4	-0.02	2173.4	-0.29
5	2242.65	-0.07	2165.5	-0.08
6	2249.9	-0.07	2157.4	0.00
7	2257.4	+0.24	2148.95	-0.17
8	2264.65	+0.41	2140.85	+0.13
9	2271.7	+0.52	2132.3	-0.01
10	2278.3	+0.23	2123.6	+0.09
11	2285.1	+0.23	2115.1	-0.04
12	2291.6	+0.04	2106.5	+0.07
13	2298.3	+0.10	2097.9	+0.23
14	2305.05	+0.31	2088.9	+0.11

In the 3.3μ region, there are two fundamentals, an overtone, and a band of normal methane, the latter appearing with small intensity. The parallel band, ν_1 , has its center at 2983.0 cm^{-1} , no fine structure being observed because of the overlapping. The perpendicular band, ν_2 , at 3031.0 cm^{-1} , has a very strong narrow center as if all the zero branches fall close together. The overtone, $2\nu_4$, is at 2923 wave numbers, being displaced and intensified by resonance interaction with ν_1 . Measurements were taken at three pressures (Fig. 6) as given in Table V.

An attempt was made to locate some of the overtone and combination bands but due to the small amount of gas available, none were observed.

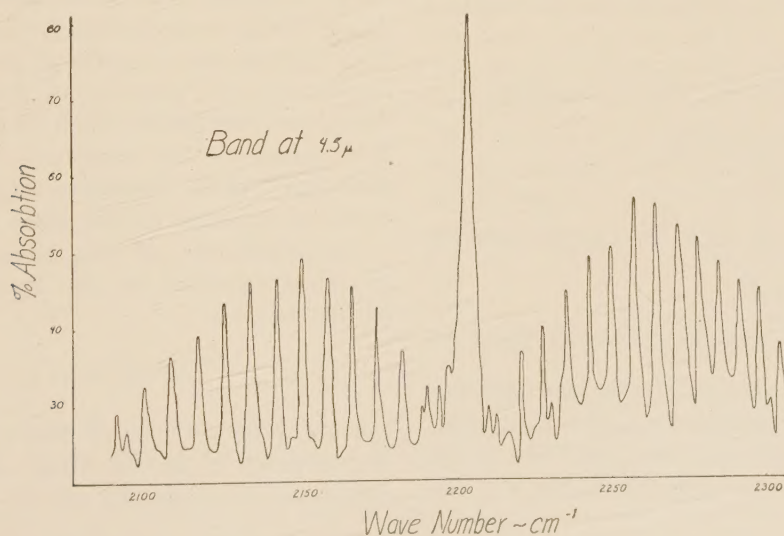


FIG. 5.

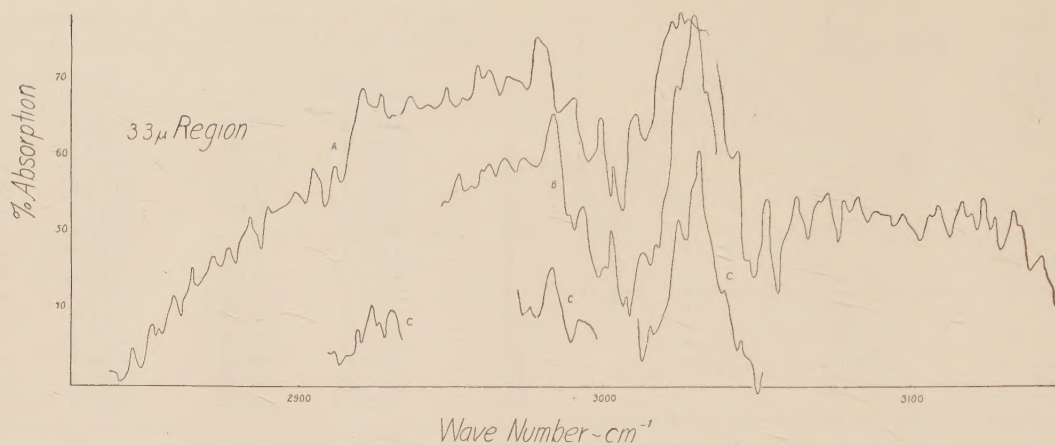


FIG. 6.

TABLE V. Experimental data for the various bands.

BAND	CELL	PRESSURE (mm Hg)	SLIT WIDTH (cm ⁻¹)	INTERVAL BETWEEN READINGS (cm ⁻¹)
Exploring				
Run	Short	700	0.7 to 1.5	0.55 to 1.4
ν_5	Long	180	0.65 to 0.9	0.6 to 0.8
ν_6	Long	180	0.9 to 1.3	0.85 to 1.05
ν_4	Long	700	1.0 to 1.05	1.2 to 1.3
ν_3	Long	180	0.8 to 0.95	0.6 to 0.75
3.3 μ Region				
A	Long	180	0.7 to 0.85	1.2 to 1.45
B	Long	80	"	"
C	Short	50	"	"

INTERPRETATION OF RESULTS

From the frequencies of normal methane, it is possible to obtain two of the potential constants uniquely,¹¹

$$C/4\pi^2 = m\omega_2^2/4; \quad E/4\pi^2 = m\omega_1^2/16$$

and two in terms of a third.

$$A/4\pi^2 = 2m\mu\{\omega_3^2 + \omega_4^2 \pm [(\omega_3^2 - \omega_4^2)^2 - (8/\mu m^2)(D/4\pi^2)^2]^{1/2}\},$$

$$B/4\pi^2 = \frac{1}{16}m\{\omega_3^2 + \omega_4^2 \mp [(\omega_3^2 - \omega_4^2)^2 - (8/\mu m^2)(D/4\pi^2)^2]^{1/2}\}.$$

By substituting any one of the observed frequencies into the equations for methyl deuteride,⁶ it is possible to determine the fifth. The results of this calculation are given in Table VI. The

TABLE VI.

FREQUENCY	D	COMPUTED CONSTANTS (10 ⁵ dynes/cm)				E
		A	B	C		
1156	1.323	7.485	0.4377	0.34047		0.3130
1307	1.328	7.281	0.4292	0.34047		0.3130
1477	Imag.	—	—	0.34047		0.3130
2205	1.328	7.304	0.4302	0.34047		0.3130
2983	-0.051	3.026	0.6714	0.34047		0.3130
3031	Imag.	—	—	0.3405		0.3130
Dennison and Johnston	1.278	7.670	0.476	0.341		0.313

constant D is very sensitive to the value of the selected frequency as can be seen by recomputing the frequencies from any one of the three closely agreeing sets of constants. The results do not differ from the observed values by more than twenty wave numbers, yet the observed frequencies give negative or imaginary values. The three frequencies which do not give acceptable values for the constants are those which take part in a resonance interaction which would be expected to shift them somewhat.

The coefficient of the linear term in the empirical equation for the rotation lines of a parallel band is

$$B = h/4\pi^2 c I_A.$$

For the 2205 cm⁻¹ band, this was 7.714. Thus the moment of inertia about an axis perpendicular to the symmetry axis is

$$I_A = 7.166 \times 10^{-40} \text{ g cm}^2.$$

¹¹ J. Rosenthal, Phys. Rev. **46**, 730 (1934).

Assuming the regular tetrahedral structure, this gives

$$\begin{aligned} \text{H-H distance} &= 1.785 \times 10^{-8} \text{ cm} \\ \text{and C-H distance} &= 1.093 \times 10^{-8} \text{ cm.} \end{aligned}$$

From this, the moment of inertia about the symmetry axis (which is the same as for normal methane) is computed to be

$$I_C = 5.298 \times 10^{-40} \text{ g cm}^2$$

as compared to

$$I_C = 5.47 \times 10^{-40} \text{ g. cm}^2$$

found by Dennison and Johnston.⁷

Teller¹² has shown that for an axially symmetric molecule, the rotational energy has the form

$$W = J(J+1) \frac{h^2}{8\pi^2 A} + \left(\frac{1-\zeta}{C} - \frac{1}{A} \right) \frac{K^2 h^2}{8\pi^2},$$

where ζ is the angular momentum due to the vibratory motion alone. Thus the spacing of the zero branches for a perpendicular band is given by

$$\Delta\nu = (h/4\pi^2)((1-\zeta)/C - 1/A).$$

Since the moments of inertia have been calculated and the spacing observed, the values of the interaction factors can be computed. It has also been proved that the sum of the factors for all three of the bands is independent of the force constants, and for this case should be one-half the ratio of the moments of inertia.

$$\Sigma \zeta_i = I_C / 2I_A = 0.370.$$

No possible combination of the ζ 's gives this sum, the best selection being

$$\begin{aligned} \zeta_6 &= 0.625 \text{ to } 0.692, \\ \zeta_4 &= -0.218 \text{ to } -0.312, \\ \zeta_2 &= 0.261 \text{ to } 0.213, \end{aligned}$$

giving the sum

$$\Sigma \zeta_i = 0.668 \text{ to } 0.593.$$

The resonance interaction between $2\nu_4$ and ν_2 would probably affect the values of these constants somewhat but would not be expected to produce such a large change.

CONCLUSION

Having observed the fundamental vibration frequencies of methyl deuteride, as well as the rotational structure of some of the bands, it was possible to compute the moments of inertia and internuclear distances and to obtain the range of values of the rotation-vibration interaction factors. Also the potential constants were evaluated.

Such complete results are possible only for this molecule or similar ones, where the determination of one moment of inertia makes it possible to calculate the other one. The differences between observation and theoretical predictions can be traced to a resonance interaction which has not been taken into account in the theoretical calculations.

We wish to thank Dr. Dennison and Mr. Johnston for conveying to us the results of their calculations which greatly facilitated the correct identification of the bands. The materials for this investigation were purchased from a grant of the Faculty Research Fund of the University of Michigan.

¹² Teller, *Hand- und Jahrbuch des Chem. Physik* (1934), Vol. 9, p. 125.



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